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A Factor Model of the Relationship between Stream Sediment Geochemistry and Adjacent Drainage Basin Lithology, Medvednica Mt., Croatia

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Key words: Stream sediment, Lithology, Drainage basins, Geochemical composition, Factor analysis, Medvednica Mt., Croatia.

Abstract

A mathematical model is constructed to relate the geochemical composition of recent stream material in a number of catchments on Medvednica Mt. to a broadely defined bedrock lithology which represents the parent material for the former. It is a system based factor model, which synthesizes eight lithological and 25 geochemical variables (major, minor and trace elements), reducing their relationships to six geologically meaningful factors. Five of these divulged a definite relationship between geochemistry and lithology. These are labelled as follows: factor of metamorphic rocks; factor of igneous rocks; factor of Tertiary carbonate rocks; factor of parametamorphic rocks and factor of Mesozoic carbonate rocks. Two lithologies; the Mesozoic clastic rocks and Quaternary sediments showed no clear association to any of the factors. Alternatively, one of the factors (F2) can be identified as "non-lithologic" indicating other, perhaps anthropogenic, contributions to the stream sediment geochemical composition.

1. INTRODUCTION

As a convenient medium for geochemical mapping the stream sediment represents a silty fraction (clay to fine-grained sand) transported and deposited in a recent stream channel. This sampling medium is still mostly preferred, particularly in areas with temperate climate and a dense drainage network because its geochemical composition is regarded as the most informative for regional reference purposes, not only in the domain of mineral exploration, but also in the area of pollution assessment (DARNLEY et al., 1995). It is well known that the petrographic, mineralogical and geochemical composition of such a composite sample, if taken in an uninhabited area, roughly reflects the bedrock lithology upstream from the sampling site, anthropogenic influences being low or absent.

Due to the specific geologic fabric, with a prevalence of various types of non-carbonate rocks, a well dissected landscape with dense drainage network has been developed into a distinguishing feature of the Medvednica Mt. Its numerous valleys offer plenty of stream material for reconnaissance geochemical surveys and various regional studies. However, the abundant lithological diversity may prove to be a disadvantageous feature as it results in progressive mixing of the eroded and transported bedload material due to the subsidiary stream channels downstream. As a consequence, the geochemical composition is charged with "noise" which renders interpreting the provenance of source material considerably difficult. Some authors (e.g. OTTESEN et al., 1989) also draw atttention to the opposite effect in the case of long and narrow valleys without tributaries, when stream sediment samples taken at intervals along the valley are no more than replicas of the same material from the same source, with no new geochemical information.

The study area abounds with both examples. In order to reconcile these extremes and elucidate the relationships between geochemical composition of the stream sediment samples and bedrock lithology underlying the sampled drainage basins we offered an approach based on multivariate statistics: the factor analysis with a series of factor score maps of the investigated area. This type of numerical analysis, applied to a great number of surveyed Medvednica streams (247), should also offer an additional insight into the possible technogenic and anthropogenic impacts that might be present in the stream sediment geochemistry, particularly on the southern slopes of Medvednica Mt. and its inhabited footfall areas.

2. GEOLOGICAL SETTING

The Medvednica Mt. is a prominent topographic unit in northwestern Croatia occupying an area of about 300 km^2 (Fig. 1). Its main body is formed of three parts:

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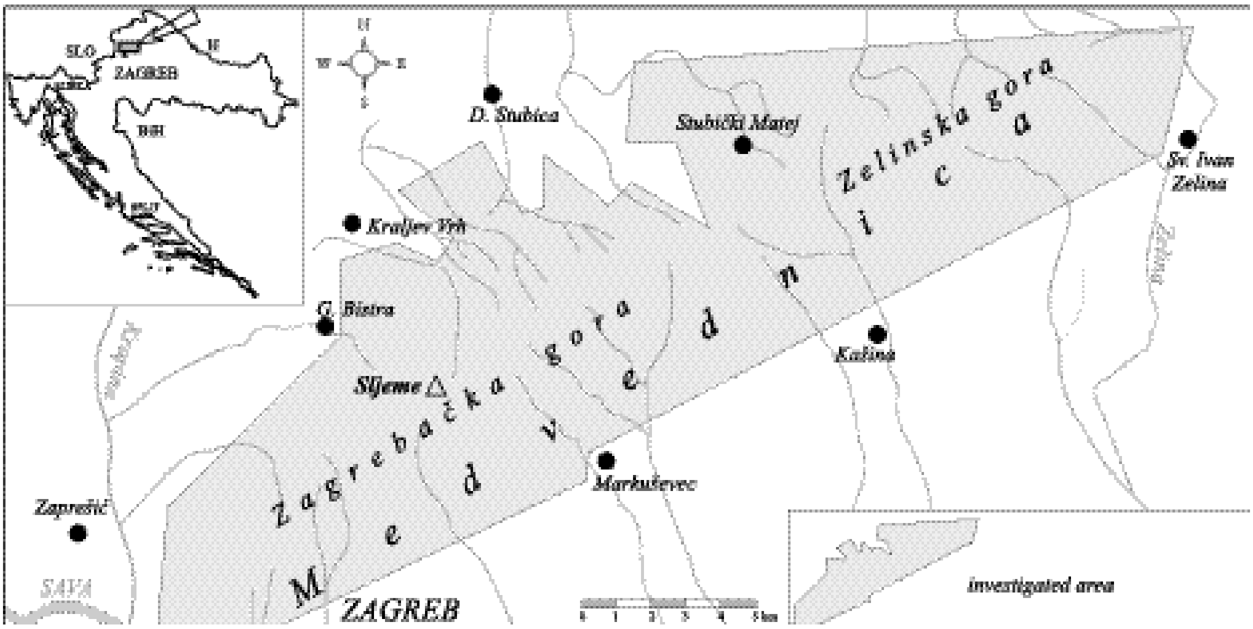

Fig. 1 Location map of the Medvednica Mt. showing delineation of the investigated area.

Zagrebačka Gora, Zelinska Gora, and the area of Hum-Šagudovec Forest. Their cores are predominantly built from the Palaeozoic and Mesozoic rocks of various origin and surrounded by younger, Tertiary and Quaternary sedimentary rocks (ŠIKIĆ et al., 1978, 1979; BASCH, 1983a, b; ŠIMUNIĆ et al., 1981, 1983) (Fig. 3).

Palaeozoic rocks are represented by orthometamorphites and parametamorphites of Silurian-Devonian age, and weakly metamorphosed rocks of supposed Lower Permian age. According to recent investigations, some protoliths comprising a portion of this metamorphic complex are assigned to the Triassic period (ĐURĐANOVIĆ, 1973; BELAK et al., 1995).

The Mesozoic of Medvednica consists of the Lower Triassic clastic rocks, Middle to Upper Triassic carbonates, as well as carbonates of Triassic-Jurassic and Jurassic-Cretaceous age. The Cretaceous sedimentary rocks are predominantly represented by fine-grained clastics, while the carbonates of the "scaglia" facies appear more rarely.

The Cenozoic rocks are represented by Tertiary (portions of Palaeogene and Neogene) sedimentary rocks and Quaternary sediments. The former predominantly consist of fine-grained clastic rocks and marls, except for the Badenian and Pannonian rocks which can be categorized as limestones (mostly calcarenites). The lithological column for the Quaternary is characterized by recent silts, sands and gravels deposited in the stream valleys, as well as sediments in the sinkholes within the area of Ponikve.

A number of various ore occurrences are disseminated over the entire area of Medvednica Mt., particularly in its central parts. In the belt of predominantly orthometamorphic rocks (green orthoschists), several occurrences of magnetite-haematite are recorded. There are also sections with great bodies of barite. The lead-zinc ore occurences which contain admixtures of silver and copper are associated with partly recrystallized limestones and dolomites (marble) in the parametamorphic complex (ŠINKOVEC et al., 1988).

2.1. Lithologic units

Due to geotectonic evolution of the terraine of Northwestern Croatia, the Medvednica Mt. portrays a complex geological structure, obvious from a variety of lithologic units formed over a large span of time (Siluro-Devonian to Quaternary) concentrated in a relatively small area. Therefore isolating the different rock masses into compact and definite lithologic units is an arduous endeavour. The composition of eight more or less closed lithologic units allowed all types of rocks to be represented within the smallest possible number of classes, while providing the maximum information. We restricted the criteria for classification of rocks into different groups to two items: 1) their origin (igneous, sedimentary and metamorphites); and 2) their age. Here, we further subdivided sedimentary rocks into two classes (clastic and carbonate) disregarding the mechanism and environment of sedimentary processes as these would considerably increase the number of created groups and further aggravate the interpretation of results in this phase of the investigation. A problem also occured with the correct separation of various rocks into "pure" groups (e.g. parametamorphites from orthometamorphites, calcareous clastic rocks from carbonates, etc.) so that each lithologic unit is pre-labelled "predominantly".

According to the above considerations we synthesized eight lithological units on the Medvednica Mt. These comprise: 1) Parametamorphic rocks, 2) Orthometamorphic rocks 3) Igneous rocks, 4) Mesozoic clastic rocks, 5) Tertiary clastic rocks, 6) Mesozoic carbonate rocks, 7) Tertiary carbonate rocks, 8) Quaternary sediments.

Metamorphic rocks of Siluro-Devonian and Lower Permian ages are classified into the group of parametamorphites while the greenschists, amphibole schists, metagabbros and metadiabases of the same age are assigned to the orthometamorphite group.

The lithologic unit of igneous rocks is represented by quartzdiorites, diorites and quartzkeratophyres of Upper Palaeozoic age, as well as gabbros, basalts, diabases, and spilites of Mesozoic age.

The group of Mesozoic clastic rocks includes the Lower Triassic as well as Lower and Upper Cretaceous sedimentary rocks of different structure and texture (predominantly sandstones and siltites regardless of their composition, together with shales and, more rarely, marls).

Various rocks of Palaeocene, Ottnangian, Karpatian, Upper Pontian, and Plio-Quaternary ages belong to the group of Tertiary clastic rocks. Some classification problems occurred with marls which comprise a considerable portion among other members. This refers to the lack of relevant references about the origin of the carbonate component in these rocks which may be clastic or chemogenic. Part is determined as sandy-silty-clayey marl or as clayey-sandy marl (ŠIKIĆ et al., 1979; BASCH, 1983b; ŠIKIĆ, 1995) which was the main reason for classifying all these sedimentary rocks as clastic.

Dolomites and dolomitized limestones of Triassic age, together with limestones and calcareous breccias are appointed to the group of Tertiary carbonate rocks.

Badenian bioclastic limestones and algal (lithothamnium) limestones, together with clayey limestones of Sarmatian and Pannonian age form the group of Mesozoic carbonate rocks.

Gravel, sand, silt and clay represent the Quaternary sediments which occupy considerably small portions of the investigated area (Fig. 3).

3. SAMPLING AND ANALYTICAL METHODOLOGY

3.1. Sample material

The main objective of analyzing the stream sediments of Medvednica Mt. was to obtain the baseline concentration values for a set of chemical elements that would be useful as a database in regional comparisons. The samples were collected according to a previously defined irregular network, with a sampling density of approximately 1 sample/km^2 (detailed survey data). In order to reduce the anthropogenic and technogenic influence on the chemical composition of stream sediment samples as much as possible, the sampling network was designed such that sample sites avoided inhabited areas. Samples were collected about 10 m upstream from the mouth of each stream in order to escape the zone of confluence, which would cause the mixing of bedload material during the season of high waters. On the sampling site, at least five grab samples of active fine grained sediment were collected from different places along a 30 m upstream section. From this material a composite sample was made weighing up to 1,5 kg. This procedure decreased the possible bias caused by local variability. In order to assure the same sedimentary conditions, sampling was carried out during the dry season. As many as 247 samples were collected (Fig. 2), over an area of about 250 km^2.

3.2. Analytical procedure

The air-dried samples were sieved to the <0,125 mm fraction, quartered and homogenized in a porcelain mortar resulting in a 10 g subsample. The stream sediment survey performed for implementation of the Austrian geochemical atlas highlighted the fraction of <0,18 mm as giving the best results for most elements (THALMANN et al., 1989).

The samples were analyzed by indictively-coupled plasma spectrometry (ICP-AES) after total hot 4 acid (HCl-HNO_3-HF-$HClO_4$) digestion at a temperature of 200° C in the ACME Analytical Laboratories in Vancouver. Digestion of refractory minerals (casiterite, wolframite, chromite, spinel, beryl, zyrcon, tourmaline, magnetite and barite) is incomplete by this admixture. Moreover, there is possible loss of As, Sb, Cr and Au by volatilization of $HClO_4$. Si is totally volatilized by HF.

3.3. Accuracy and precision

Samples were analyzed for 35 elements. In more than 50% of cases the measured values for several elements such as molybdenum, silver, uranium, gold, cadmium, antimony, bismuth, wolfram, berylium and tin fell below the detection limit which is why these are ommited from consideration. A total of 25 elements were accepted for further analysis.

The analytical accuracy was checked using the international geological standards: GXR-5 and SJS-1 (recommended values by GOVINDARAJU, 1989; ABBEY, 1983; GLADNEY & BURNS, 1984). For most determined elements, except aluminium and zirconium, the accuracy proved acceptable in the first approximation.

Precision was monitored by blind determination of 32 samples in a series of 20 pieces and statistically expressed as the variation coefficient (%). The laboratory errors were 37% for arsenic, 17% for lead and 11% for niobium. For the rest, the coefficient values are below 10% which is considered satisfactory.

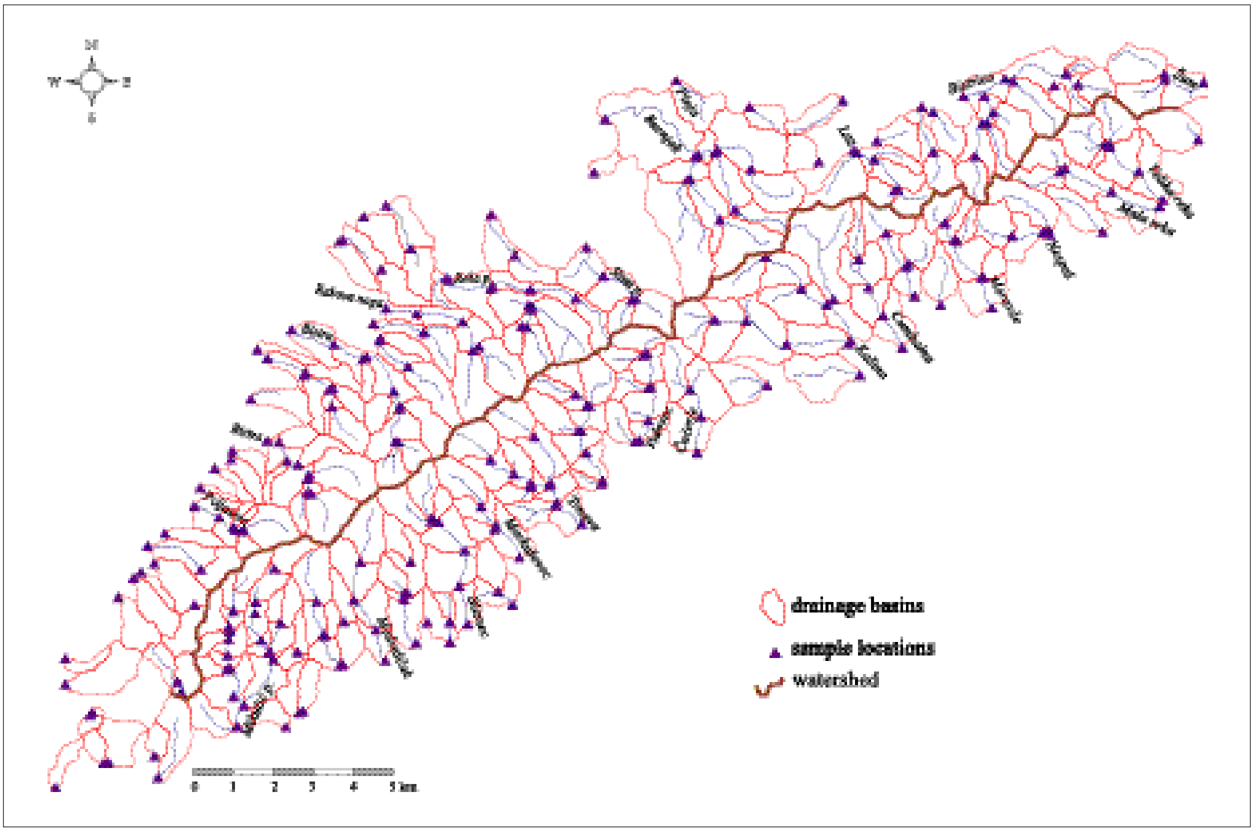

Fig. 2 Sample localities, streams, and drainage basins in the investigated area.

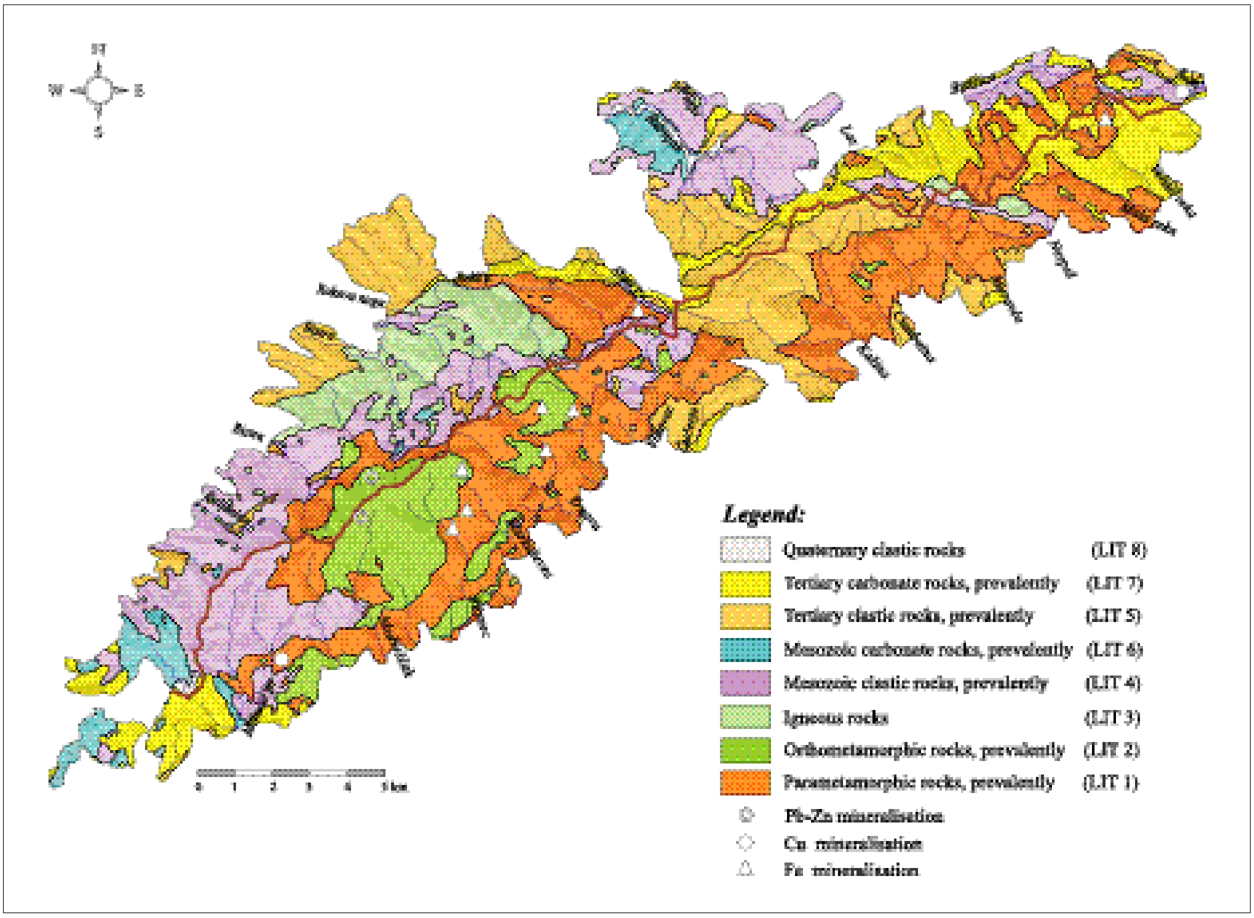

Fig. 3 Generalized lithological map as derived from ŠIKIĆ et al., 1978; BASCH, 1983a; ŠIMUNIĆ et al., 1981 - schematised and simplified.

4. STATISTICAL TREATMENT

4.1. A database

In this study 247 samples were collected from the streams of the Medvednica Mt. For each sample, 33 descriptors consisting of eight lithological and 25 geochemical variables were observed and included in the factor analysis. Inasmuch as the analysis of reconnaissance geochemical-geological data substantially makes use of a reach-scale pattern of variability, it was only natural to relate the sampled stream segments with the surrounding catchment area. This approach enabled lithological quantification within each drainage basin and the subsequent utilisation of this data to account for geochemical variation in the study area. The drainage basins were delineated in such a way that each basin segment corresponded to the area upstream and upslope of each sampling site, terminating at the location of the next sample site and at the top of the watersheds. Therefore, many of the basins were nested, with successive samples being taken down the same stream. However, the absence of a hierarchical ordering prevented a close inspection into the controls over downstream dilution of possible anomalies, because mixing of lithologically different bedload from subsidiary streams inevitably resulted in a certain amount of "noise". Such samples were clearly not independent of one another both in a geochemical and statistical sense as they would have been if the stream segments belonged to the same order.

Variables

The effects of lithology, conveyed through the lithological variables, were defined as a percentage of the drainage basin area which is occupied by a dominant rock type (ROSE et al., 1970; BONHAM-CARTER et al., 1987; PEH, 1992). As the bedrock lithology of Medvednica Mt. comprises a variety of igneous, sedimentary and metamorphic rocks of different stratigraphic and tectonic settings, a simplified representation of lithology with as little as possible loss of useful information was necessary. For this purpose map data were scanned from the geological map of the Medvednica Mt. which, in turn, was compiled from the geological map of Croatia (scale 1:100.000), sheets of Zagreb (ŠIKIĆ et al., 1978), Ivanić-Grad (BASCH, 1983a), and Varaždin (ŠIMUNIĆ et al., 1983). Thus, a generalized lithological map was generated containing only eight lithological units which were broadly related to the corresponding stratigraphic nomenclature (Fig. 3). These units were further utilized as lithologic variables which were specified as follows: LIT1 - predominantly parametamorphites; LIT2 - predominantly orthometamorphites; LIT3 - igneous rocks; LIT4 - predominantly Mesozoic clastic rocks; LIT5 - predominantly Tertiary clastic rocks; LIT6 - predominantly Mesozoic carbonate rocks; LIT7 - predominantly Tertiary carbonate rocks; LIT8 - Quaternary sediments.

The geochemical variables included a selection of 25 elements - eight major and 17 minor and trace elements. The data required transformation with most of the elements in order to meet the assumptions of normality. For these elements $\log_{10}$ and $\log_2$ logarithmic transformations were used instead of the original data to reduce the skewness of distribution. Only Fe, Al and K among major elements, and Mn, Ba and La among minor and trace elements are characterized by normally distributed data so that they were left non-transformed.

4.2. Factor analysis

The exploratory factor analysis is a powerful mathematical and statistical tool in handling a great number of numerical data. As a multivariate method, it facilitates the reduction, transformation and organization of the original data by the use of intricate mathematical techniques, which eventually results in a simple form of factor model. Thus, a factor model represents, in a sense, a minimum or reduction model which explains correlations among observed data in as few terms as possible, ignoring minor influences and non-linear effects that may be present (MIESCH et al., 1966). In such a way it resolves the multivariate relations among variables in their correlations with a number of mutually uncorrelated, and hence independent, factors (DAVIS, 1986), and portrays them in the space of the least possible dimensions. In other words, factor analysis creates the minimum number of new variables which are the linear combinations of the original ones with the same amount of information.

If the original variables have significant linear intercorrelations, the first few factors will account for a large part of the total variance (McCAMMON, 1966). These then may be used to describe variation as observed in the original data and, subsequently, to explain the processes underlying the structure of the mathematical model. Finally, for each sample, the factor scores can be computed which replace the values of the original variables. These characterize each sample and thus may be used in any subsequent classification or correlation analysis. Factor scores can be particularly useful in creating the factor maps which display the areal distribution or influence of a particular factor, thus indicating predominant control of some natural process or processes.

5. RESULTS

5.1. Selection and rotation of factors

Inasmuch as the factor analysis had been used as an exploratory method in geochemical investigations, the number of factors essential to the interpretation of the factor model was specified during the analysis. No assumptions about the investigated area with regard to the relationship between lithological types and stream

FACTOR	EVAL	%EVAL	%cum
F1	7.87	23.15	23.15
F2	3.99	11.73	34.88
F3	3.25	9.56	44.44
F4	2.69	7.91	52.35
F5	2.23	6.56	58.91
F6	1.73	5.09	64.00
F7	1.61	4.72	68.72
F8	1.46	4.31	73.03
F9	1.43	4.20	77.23

Table 1 Eigenvalues and respective factors (after rotation).

sediment geochemistry has been established prior to analysis. This presented some problems as the primary idea of associating individual factors with specific lithology has not met the necessary criteria for factor extraction such as the variance rule, or Kaiser's eigenvalue>1 criterion, in particular. The two criteria effectively strain on the side of a plenitude of significant factors, indicating that the system's variability is much dispersed through the system due to some qualities ingrained in the nature of data. In both cases, using the usual cutoff of 75% of total variance, or the $\lambda>1$ value (Table 1), the nine factors could be retained, which is a solution that exceeds even the total number of lithologic variables. These examples raise certain ambiguities concerning a meaningful and clear-cut geological interpretation of the computed factor model. In contrast, according to the scree test as the third criterion for factor significance (Fig. 4), the three or four factor solution will emerge as sufficient. This, conversely, does not leave enough room for defining a clear affinity between lithology and stream sediment geochemical composition.

In the search for an optimum solution in the factor selection it was mandatory to reconcile these criteria with the concept of the system under investigation. Thus, a cautious, but safe, compromise was chosen to overfactor rather than to underfactor the data in analysis. This took into account the general consensus of opinion prevailing among researchers (CONWAY & HAYNES, 1973) that it is better to rotate too many factors than too few because the former case does not influence the structure of general factors accounting for greater portions of variance.

Pursuing the above suggestions, the nine factors were selected and rotated but only the first six were retained for further examination (Table 1). The last three factors were ommited from further consideration due to the lack of sensible geological meaning that could be attached to them. These can be considered as a "residual heap" that should be left without explanation as only one or two geochemical variables, without due lithology, load highly on each factor.

5.2. A model

The accepted solution is essentially a conceptual, systems-based model the primary objectives of which were: a) to establish the relationship between the bedrock lithology and geochemical composition of the stream sediments on the Medvednica Mt., and; b) to elucidate, if possible, the natural processes underlying that relationship. The model is presented in the form of a varimax rotated factor matrix (Table 2) in which the six factors explain almost two thirds of the total system variability. As can be seen from Table 1, although the first factor (F1) predominates and accounts for almost twice as much of the total explained percentage variance as the second (F2), the other factors show a slow decline in magnitude which is a sure indicator of weak

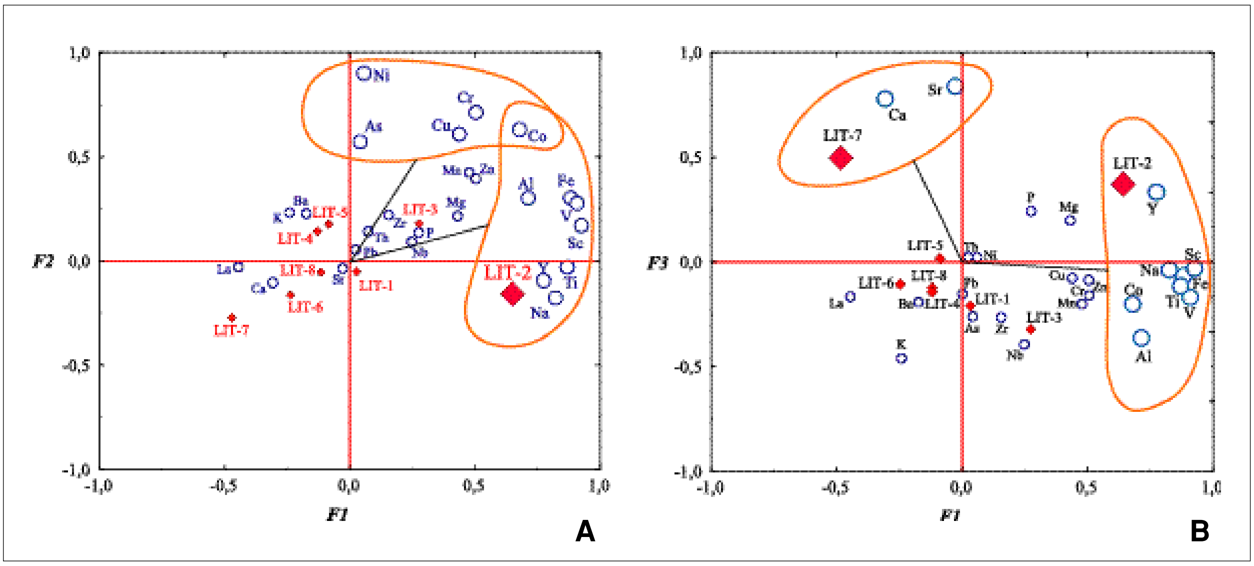

Fig. 4 a) Plot of loadings on the first and second varimax rotated factors; b) plot of loadings on the first and third varimax rotated factors.

	FACTORS						
VAR	F1	F2	F3	F4	F5	F6	h^2
LIT1	-0.01	0.06	0.22	-0.16	**0.81**	-0.15	0.75
LIT2	**0.62**	-0.14	-0.19	*0.41*	0.08	0.09	0.62
LIT3	0.26	0.17	*-0.40*	*-0.45*	-0.10	-0.04	0.49
LIT4	-0.13	0.18	0.19	-0.11	**-0.75**	-0.15	0.69
LIT5	-0.06	0.13	0.02	0.02	-0.02	-0.07	0.03
LIT6	-0.22	-0.18	-0.02	-0.12	-0.05	**0.87**	0.85
LIT7	*-0.42*	-0.32	-0.05	*0.49*	-0.01	-0.11	0.53
LIT8	-0.04	-0.13	-0.05	-0.06	-0.18	0.36	0.19
Fe	**0.86**	0.38	-0.09	-0.09	0.14	0.02	0.91
Ca	-0.34	-0.12	-0.35	**0.70**	0.16	0.22	0.82
Mg	0.38	0.29	-0.22	0.14	0.07	**0.69**	0.78
Ti	**0.91**	-0.01	-0.06	-0.14	-0.07	0.00	0.85
Al	**0.70**	0.36	0.25	-0.28	0.09	-0.14	0.78
Na	**0.81**	-0.12	-0.13	-0.05	0.14	-0.19	0.74
K	-0.21	0.21	**0.68**	-0.30	0.09	-0.19	0.69
P	0.29	0.11	0.28	0.31	**0.66**	0.01	0.71
Cu	0.40	**0.69**	0.12	-0.02	-0.01	-0.01	0.65
Pb	-0.08	0.10	0.19	-0.06	-0.00	-0.04	0.06
Zn	**0.50**	0.43	0.17	0.00	0.23	0.06	0.53
Ni	-0.00	**0.90**	0.09	0.03	-0.09	-0.03	0.82
Co	**0.64**	**0.69**	0.04	-0.19	0.01	-0.05	0.92
Mn	0.49	0.48	0.14	-0.14	0.14	0.05	0.53
As	0.03	0.45	-0.11	-0.29	0.31	-0.18	0.43
Th	**-0.54**	0.08	**0.71**	-0.18	0.04	-0.08	0.84
Sr	-0.05	-0.05	-0.17	**0.84**	-0.03	-0.18	0.78
V	0.88	0.35	-0.11	-0.18	-0.01	0.03	0.94
La	-0.38	-0.05	**0.80**	-0.01	0.16	0.03	0.81
Cr	0.44	**0.74**	-0.06	-0.18	-0.08	-0.03	0.79
Ba	-0.13	0.17	**0.51**	-0.02	0.09	-0.18	0.35
Zr	0.15	0.38	0.30	-0.27	-0.41	0.10	0.51
Y	**0.80**	-0.05	-0.14	0.30	-0.05	0.15	0.77
Nb	0.35	0.05	**0.65**	-0.32	-0.17	0.00	0.68
Sc	**0.89**	0.24	-0.23	-0.04	0.08	-0.04	0.91

Table 2 Varimax rotated factor matrix.

interdependence among the observed properties (Fig. 4). Generally, the dominance of a single factor implies that the constraints operating within a system greatly decrease as the components tend strongly to cooperate toward the equilibrium conditions (CHORLEY & KENNEDY, 1971; ONESTI & MILLER, 1974). However, this is not the case here judging from the slight drop in eigenvalue manifested from the second factor on, which suggests a complex influence posing mutual restraints within a system. It is inextricably woven into the geological (lithological in particular) fabric of the investigated area, but may also ensue from the accepted non-hierarchical pattern of the drainage basin network to which all studied relations converge.

5.3. Labelling the factor axes

Among the six rotated factors the first factor F1 accounts for 23.15% of the total system variability. It is a monopolar factor (or slightly bipolar as far as Th is concerned) which is essentially composed of variables positively correlating orthometamorphic lithology (LIT2) to the major lithophile elements such as Fe, Ti, Na and Al. A group of minor and trace elements including V, Co, Th (negatively associated), Zn, Mn, as well as Sc and Y, also load on this factor. Some of these elements - particularly Co - share their variability with the second factor, which indicates that they may also derive their origin from some source other than orthometamorphic rocks eroded by the sampled streams. Such a case implies a kind of interdependence between the two factors which are mathematically orthogonal (and thus independent) but conceptually related due to some unknown nonlinear responses among a number of system variables (NORRIS, 1971). This is clearly suggested by a typical "horse-shoe" plot with Co and Zn as binding variables (Fig. 4a). There is also a slight interdependence with the third factor owing to the relatively high loadings of Th on both F1 and F3. Despite the peculiar behaviour of the trace elements, the firm correlation between major elements and lithology can be established so that F1 can be properly referred to as the **factor of orthometamorphic rocks.**

The second rotated factor F2 explains a further 11.73% of the total information in the data matrix. It is largely concerned with positive associations within a set of trace elements of litho-chalcophile characteristics, such as Ni, Co, Cr, as well as chalcophile Cu (Zn and As), which occur mostly in the form of sulphides (ore minerals). A notable absence of the major elements, as well as non-appearance of a direct link with any of the lithologic variables (Table 2) suggest an undefined type of parent rocks as the source of their origin. Some unclear ties with lithology can be deduced from the shared loadings of Co (and, less characteristic, of Mn, Zn and Cr) on both F1 and F2, which hints at orthometamorphic primary rocks, bearing scarce sulphidic ore veins, as their partial provenance. Also, possible effects of industrial contamination cannot be ruled out due to a number of active quarries on the footslopes of the Medvednica Mt. Owing to its lithological ambiguity, the second factor F2 should be labelled provisionally as the **non-lithologic factor** .

The third factor F3, explaining a further 9.56% of the total variance, is of a bipolar nature on the grounds of the negative relationship that unites the set of geochemical variables K, Th, Ba, La and Nb with lithological variable LIT3 standing for igneous rocks. This is a rather peculiar situation as one must associate the occurrence of these elements with the apparent absence of indicated lithology and vice versa, as though the relationship is based on mutual aversion. It is aggravated, further, by a quite unimpressive loading of LIT3 (-0,41) on this factor, which commands caution in its interpretation. Thus, a safe approach to the probable solution would be that the occurrence of the K-Ba-Th-La-Nb set is somehow limited in the range of drainage basins dominated by the igneous rocks, rather than enriched in those covered by other types of lithology, although the reasons for such behaviour remain unknown. Perhaps this picture reflects the sharp contrast between the areas of erosion and deposition reflecting the situation when, due to the geomorphologic, hydrologic, hydraulic and other drainage basin/stream channel processes, the geochemical assemblage of stream sediments finds itself in "alien lithological surroundings" downstream. Thus a "negative" image in the factor model might have been created. The similar, but much simpler, example can be encountered with F1 where all relevant geochemical variables are negatively associated with the weakly loaded LIT7 (carbonate rocks). As the orthometamorphites are the dominant lithology, no problems with factor interpretation arise in that case. Here, again, following the relationship between geochemical and lithological variables, the factor F3 could be correspondingly labelled the **factor of igneous rocks** .

With the fourth factor F4 commences a series of factors more easily explainable in terms of the relationship between geochemical composition of stream sediment samples and lithology of adjacent drainage basins. The reason for this is a considerably reduced number of variables loading significantly on each factor which greatly simplifies the factor structure. The first of these, F4, accounts for 7.91% of the total variance examined. As can be seen from Table 2, it is dominated by only two geochemical variables, namely Ca and Sr, that covary in a positive relationship with dominant lithological variable LIT7 standing for the Tertiary carbonate rocks. The explanation of this factor is, thus, straightforward and it can be readily described as the **factor of Tertiary carbonate rocks** . A weak relationship with lithologic variables LIT2 (+) and LIT3 (-) also exists suggesting that a minor portion of Ca and Sr might be derived from the orthometamorphic lithology, but essentialy from the areas devoid of igneous rocks. The joint plot with the first factor F1 (Fig. 4b) is added to portray the mathematical and conceptual independence of the first factor as opposed to the clear F1-F2 interrelationship (Fig. 4a).

The fifth factor F5, which explains another 6.56% of the total variance, is of a strongly bipolar nature with exception to earlier cases that two lithologic variables, LIT1 and LIT4, stand against each other, while the single geochemical variable P affiliates with the former. This may be interpreted as a result of enrichment with accessory phosphoric minerals, such as apatite, in the zone of predominance of parametamorphic rocks. In contrast, stream sediments collected in the area predominantly overlain by Mesozoic clastic rocks can be seen to be deficient in phosphorus. A weak loading of Zr that associates with LIT4 may be instructive as to the primary composition of the Mesozoic clastic rocks. This factor can be interpreted as the **factor of parametamorphic rocks** .

The sixth factor F6 is the last in the series of significant factors which accounts for only a small fraction (5.09%) of the total variance. This factor is the simplest of all, being highly loaded with only two variables. Its structure is marked by a high positive association between a single geochemical and a single lithological variable, which leaves no room for doubt as to the origins of this correlation. The Mesozoic carbonate rocks, notably dolomites of the Middle and Upper Triassic (LIT6), are indicated as the primary source of Mg in the stream sediment. This factor can be easily identified as the **factor of the Mesozoic carbonate rocks** .

Some variables in the model do not greatly participate in explaining the accepted factor solution. This can easily be seen from the fraction of the total variance carried by each variable, which is explicable by all six factors in the model. This value, known as communality h^2, diverges widely from variable to variable. Close examination of the factor matrix (Table 2) reveals that lead partakes in the common variance considerably less than 50% (h^2=0,50). This is also true for lithologic variables LIT5 and LIT8, which means that the Tertiary clastic rocks and Quaternary sediments do not help much in clarification of the relationship between underlying bedrock lithology and geochemical composition of the stream sediment. The reasons for geochemical variables not being "adopted" by any of the explained factors in the factor model may vary. One of them is probably built in analytical methods that set the concentration values for the elements, such as Zr for example, near the detection limit, causing the possible loss of the larger portion of a variable's innate variance. Others can truly refer to the circumstances that are inherent to the observed data, announcing that some elements, such as Pb, have little to do with the system investigated, having entered from outside, perhaps in a form of a pollutant. This, however, is not grounded in a factor model and in this stage belongs wholly to the realm of speculation.

A number of variables have moderate communalities with magnitudes vacillating around 50% of the model explanation; Mn, Zn, Cu amongst others. Hence, these partake significantly in the common solution and should not be discarded. Yet, as a rule, their loadings are scattered on two factors with greately reduced values on both, which decrease their variability in the factor explanation. Manganese is a good example, and the first two factors are notable in this sense.

6. FACTOR MAPS

After determining the geological meaning underlying the relationships among original variables, it was of interest to observe the areal distribution of variances, and possible trends hidden behind the respective factors. Thus, the construction of the factor maps proved to be essential for the geological factor study as they allowed the lithological-geochemical domains to be related to other geological characteristics in the investigated area. For each stream sediment sample a factor score was computed which represents the "amount" of a particular factor in that sample, that is, the drainage basin from which it was collected. The range of factor scores delineates the shift of this amount from the mean value expressed in units of standard deviation. In all cases, except for the sixth factor (F6), the factor scores roughly tend to be normally distributed according to the applied K-S test, and therefore the values of factor scores were grouped into eight classes. These are arranged with regard to the so-called 1σ-, 2σ-, or 3σ-rule (deviation from mean), which applies to the standard normal distribution curve of μ=0 and σ=1. The factor score value for each sample, entering one of the classes, was attached to the corresponding drainage basin and presented on the map. As can be seen from the factor maps, a simple but instructive display of drainage basins distinguishes the sections of increased or decreased "amounts" of factors over the study area. What is particularly informative about the classes is that they indicate the basins where the specific factor shows the variance which may vacillate within or outside the range of the background values. Thus, the basins falling within the limits of $\mu \pm 1\sigma$ (-1<FS<1) tend to show the background tendencies with regard to the variable assemblage loading significantly on the specific factor. Naturally, disposition of the factor scores over the "threshold", in the area greater than one (>1σ), or less than one (<-1σ) standard deviation, indicates the drainage basins where the factor scores suggest either enrichment of a particular geochemical association in relation to lithology, or its deficiency, respectively. These values can be considered anomalous in the exploratory analysis, at least as the first approximation. For a normally distributed population, factor score values higher than background, but fixed within the range of the mean plus 2σ (1<FS<2), are usually termed nonsignificant anomalies, while those greater than the mean plus 2σ (2<FS<3) can be considered as significant anomalies (ROSE et al., 1979). The values higher than 3σ are obviously outliers. These considerations also apply to the negative values, although in geochemistry the negative "anomalies" are seldom accounted for.

6.1. Description of factor maps

The significant anomalies (>2σ) for the first factor F1 are spread around the source areas of the Medvešćak, Bliznec, Markuševac and Čučerje valleys (Fig. 5). These areas are mostly composed of green orthoschists, metagabbros and metadiabase, and occasionally by amphibole schists (ŠIKIĆ et al., 1979; PAMIĆ & INJUK, 1987; BELAK et al., 1995). The major elements Fe, Ti, Al and Na, which are positive correlated to LIT2 (orthometamorphic lithology) (Table 2), are predominantly associated with ferromagnesian minerals and plagioclase in the related rocks. The minor and trace elements V, Co, Zn, Mn, Sc and Y also derive their origin from orthometamorphic rocks (the protolith is represented by basic volcanics, basic tuffs and tuffites) in the same area which, as a rule, are distinguished by the increased content of the same elements (RÖSLER & LANGE, 1976; RÖSLER 1981; PAMIĆ & INJUK, 1987). As cobalt also contributes to the factor F2 of no distinctive lithologic provenance, it may indicate technogenic pollution of the stream sediment brought about by the quarrying of basalt rock on the northwestern slopes of Medvednica. Thorium, being negatively associated in this case, possibly reveals the enhanced migration of this element from the LIT2 group of rocks due to metamorphic processes. As a result, its "accumulation" is associated with the negative anomalies (<2σ) in the low lying drainage basins on the western and easternmost parts of Zagrebačka Gora and over most of the Zelinska Gora.

The anomalies of the "non-lithologic" factor F2 are scattered in a very irregular pattern over a few drainage

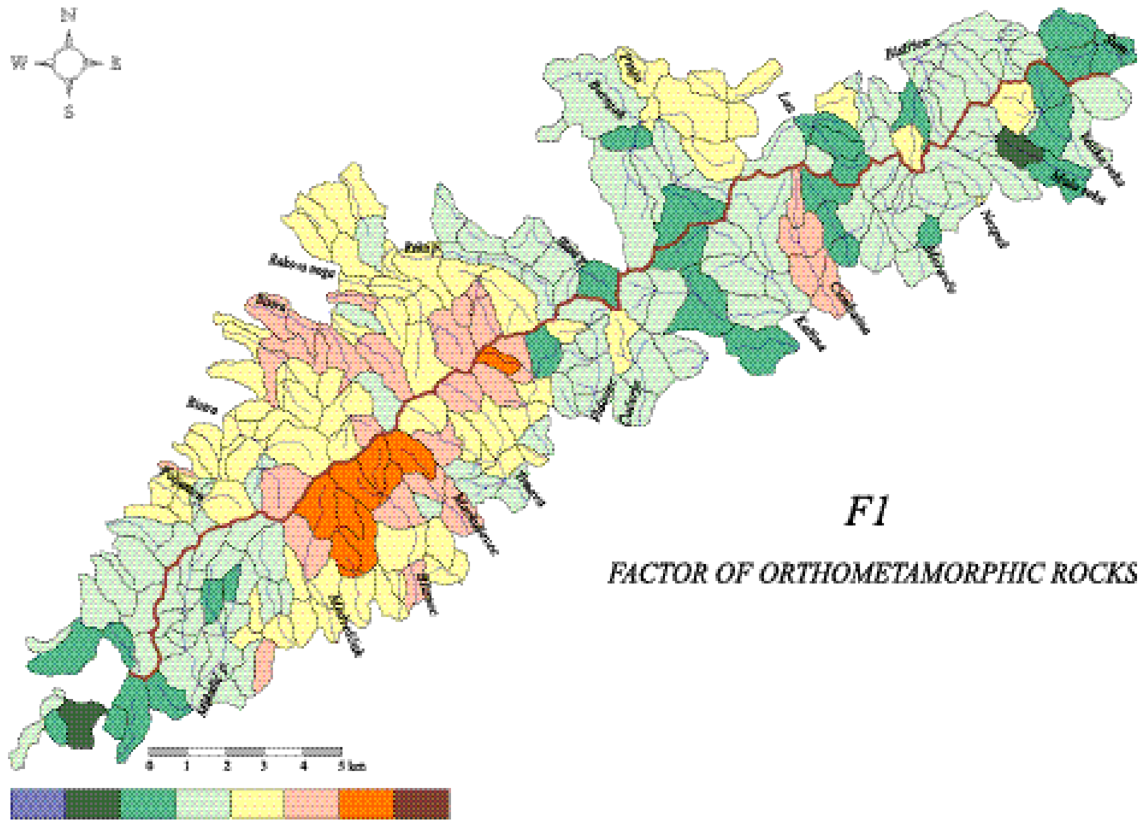

Fig. 5 Factor map of the first factor (F1).

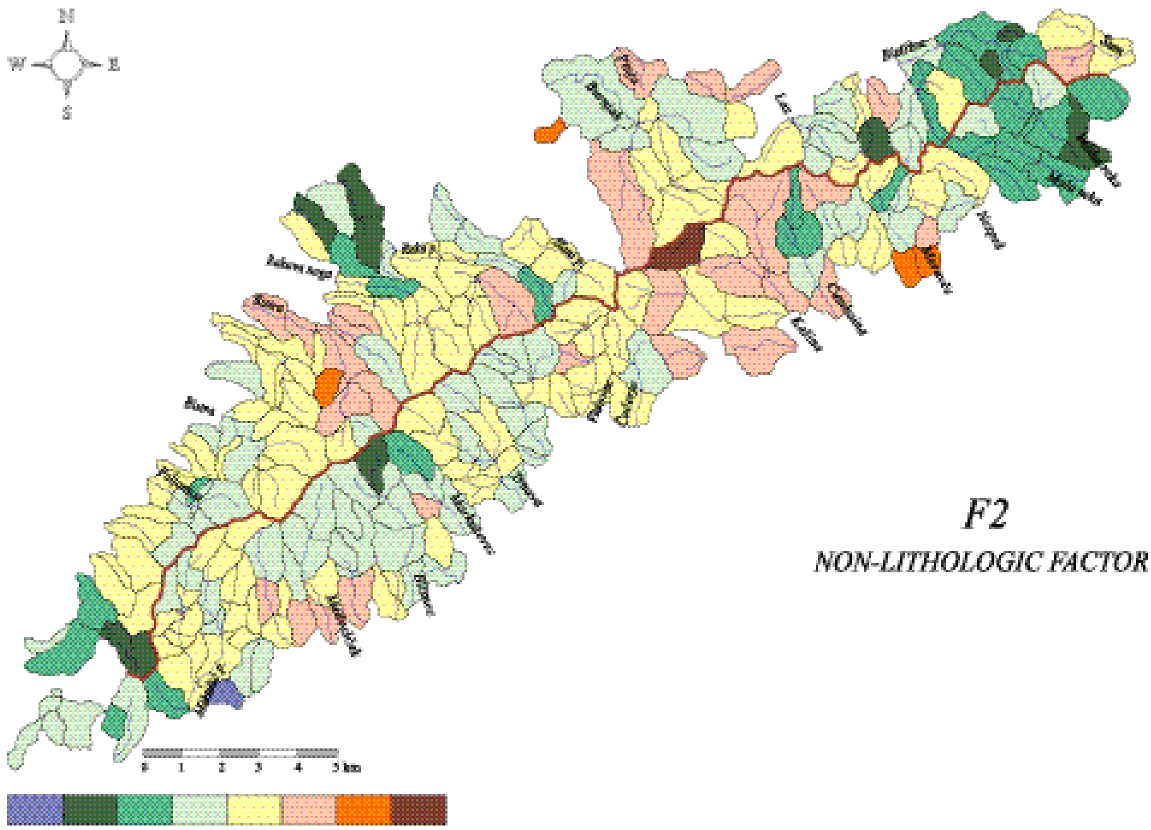

Fig. 6 Factor map of the second factor (F2).

basins: in the source area of the Kašina and Bistra streams, in the central part of the Moravče stream, and in the lower portion of the Burnjak stream (Fig. 6). The Kašina and Moravče anomalies occur in the area formed of the Tertiary clastic rocks (Ottnangian). These rocks are represented by a packet of irregularly alternating polymict conglomerates, gravels, coarse-grained sands and sandstones lying discordantly over the older rocks (BASCH, 1983a). They derive their origin from the intensively eroded Mesozoic bedrock (Upper and Lower Palaeozoic, Triassic, Jurassic-Cretaceous). Conglomerates contain, in part, pebbles of spilite, diabase and basalt (PAVELIĆ, 1998) - the basic rocks with increased content of Ni, Cr, Co, V and Cu. In addition, these rocks are also host to fragments of ultramaphites (serpentinites) (KOCH, 1904). The anomaly in the Bistra stream (Fig. 6) is very probably associated to the increased concentrations of Co and V from industrial contamination of the local area (the quarry of Kraljev Vrh).

The negative association of elements K, Th, La, Ba i Nb with lithology LIT3 (igneous rocks) on factor F3 (Table 2) is altogether expected, since the basic igneous rocks are mostly classified as LIT3. It is well known that the increased average content of K, Th, La, Ba and Nb is more characteristic for acid igneous rocks. As a consequence, it is only natural that negative anomalies can be traced on the northwestern slopes of the Medvednica Mt. which are predominantly composed of basic igenous rocks (Fig. 7). Positive anomalies of F3 are associated with catchment basins with mostly parametamorphic bedrock (southern slopes of Zagrebačka and Zelinska Mts.) and with Mesozoic non-carbonate bedrock (the Lower Triassic clastic rocks on the northwestern section of Zagrebačka Mt. and in the area of Šagudovec Forest). These indicate that the parent material for the genesis of the parametamorphite complex and later clastic rocks of the Mesozoic period might have been derived either from older, more acid igneous rocks, or from older sedimentary rocks with a higher content of minerals characteristic of acid igneous rocks.

The map of F4 displays a concentration of the highest anomalies within the cathments lying on predominantly Tertiary carbonate bedrock - bioclastic limestones and algal limestones (Fig. 8). The increased content of characteristic elements Ca and Sr obviously originates from the same complex of rocks which occupy limited patches on the westernmost tip of Zagrebačka Mt. (Badenian and Pannonian - VRSALJKO, 1999), but spreading more frequently in the zone of Šagudovec Forest and the northeastern part of Zelinska Mt. Concerning a weak positive relationship of Ca-Sr combination with a LIT2 lithology may also indicate that some portion of these elements in the stream sediment geochemistry originated in the orthometamorphic complex (e.g. plagioclases). Higher score values of 1<FS<2 indi-

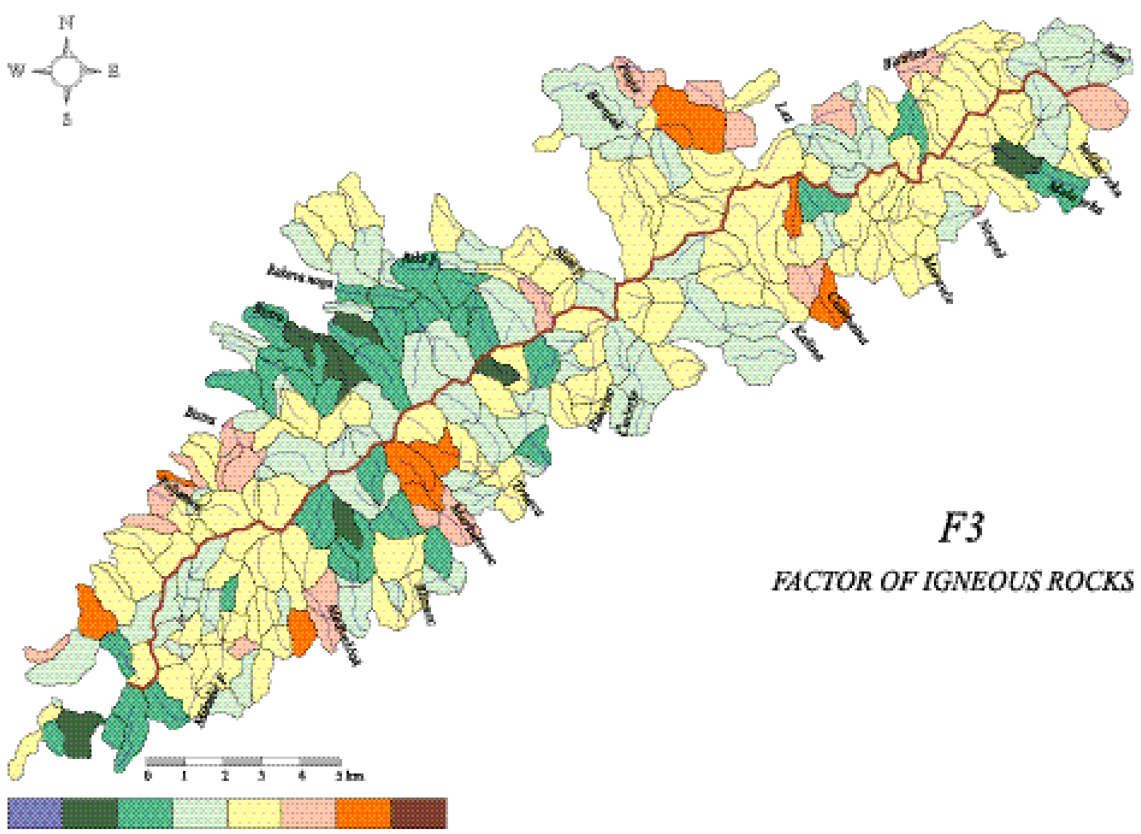

Fig. 7 Factor map of the third factor (F3).

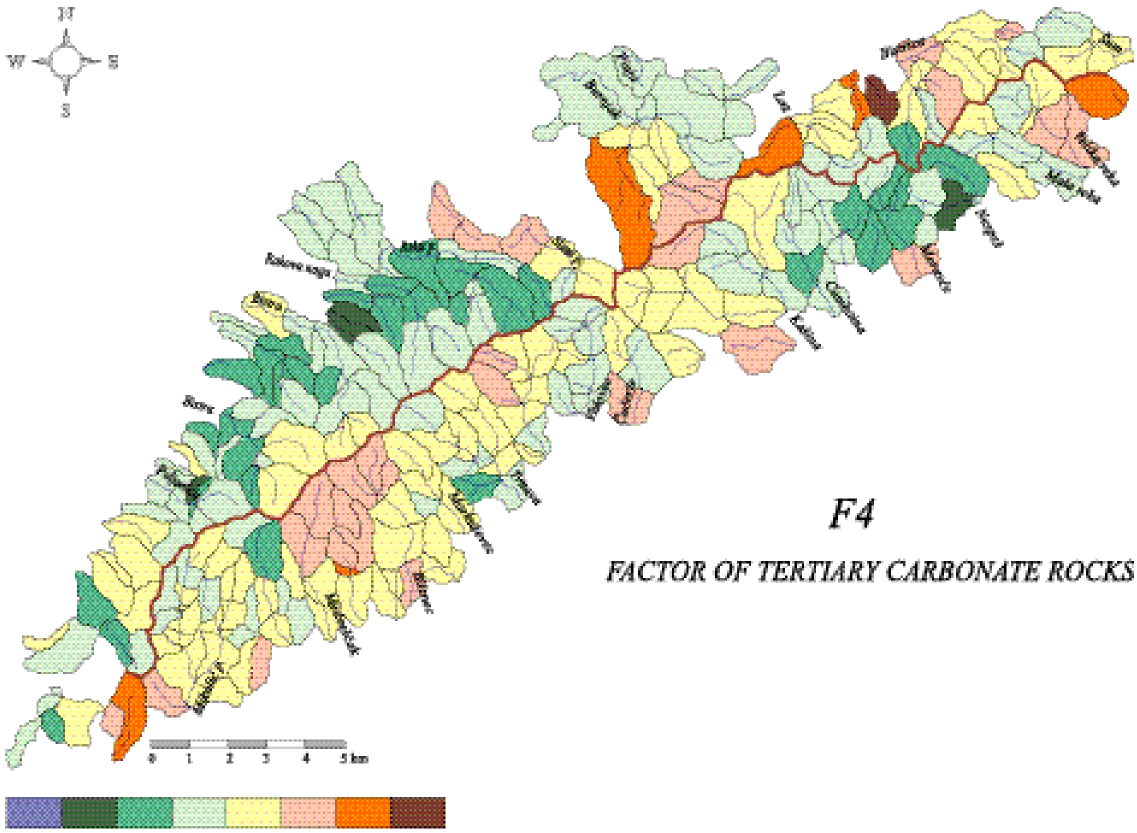

Fig. 8 Factor map of the fourth factor (F4).

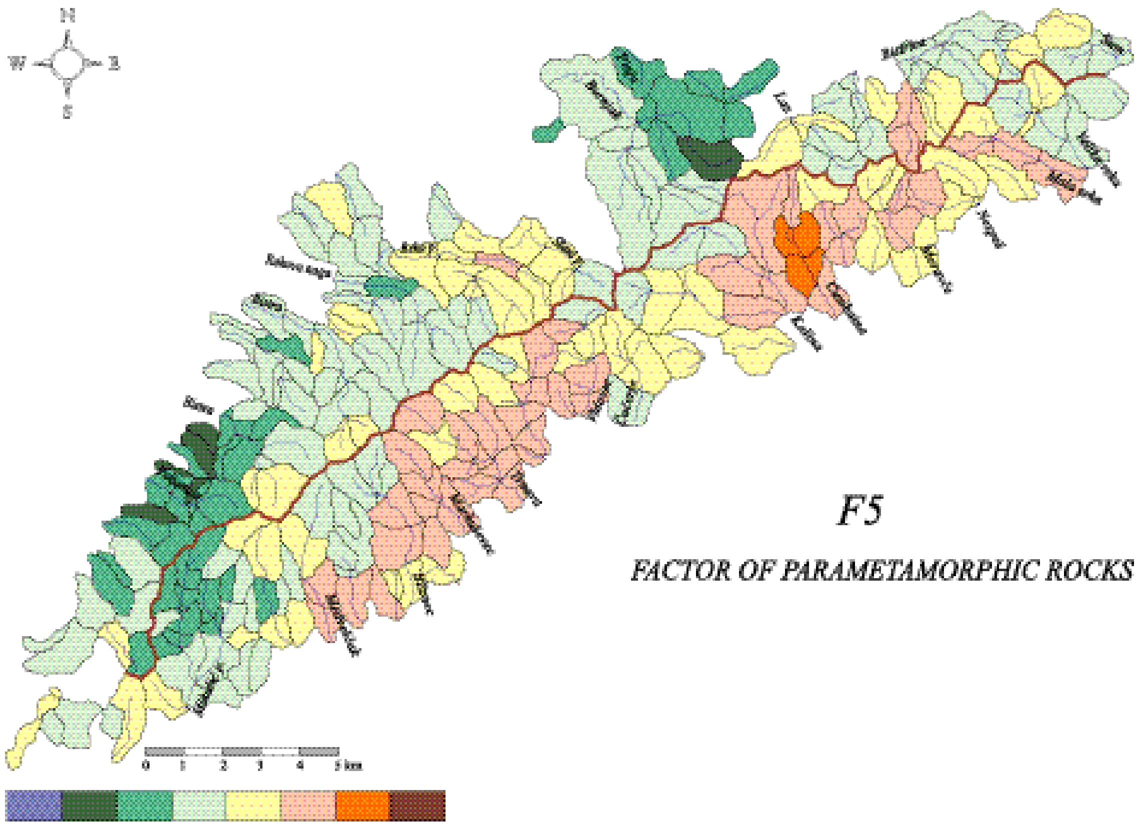

Fig. 9 Factor map of the fifth factor (F5).

cate the area with orthometamorphic bedrock.

The factor map of parametamorphic lithology displays a consistent zone on the southern slopes of Zagrebačka Mt. and Zelinska Mt. (from the Medvešćak stream on the southwest to the Mala Reka stream on the farthest northeast) with increased factor score values (Fig. 9). This area is mostly built of parametamorphic rocks, while the anomalous values in the Cumbaina valley are probably inflated due to presence of diabase veins, enriched in apatite, within the parametamorphic complex. The northwestern parts of Zagrebačka Mt. together with the Šagudovec Forest area are characterized by extremely low factor score values. These areas conform very closely to the domain of Mesozoic clastic rocks (Fig. 2). As can be seen from the factor model (Table 2) this is an area with increased concentrations of Zr in stream geochemisrty, indicating that zirconium might have been a significant constituent of the detritus material in LIT4 before its redeposition in the valleys.

The factor map of Mesozoic carbonate rocks F6 (Fig. 10) shows a few confined zones of extremely high factor score values, thinly dispersed over the northern slopes of the Medvednica Mt. These positive anomalies are associated with dolomites and dolomitized limestones of the Middle and Upper Triassic overlying the westernmost portion of Zagrebačka Mt. (Ponikve) and the Šagudovec Forest area. For the most part of Medvednica Mt. the factor scores are evenly distributed (-1<FS<1) indicating that Mg partakes in all lithologies (except LIT6) with low variability.

7. CONCLUSIONS

Many regional and local studies based on extensive use of stream sediment as the most convenient sample medium have been orientated to mineral exploration and contamination assessment. More rarely, they were focused on some particular topic of more local significance, such as the relationship between the stream sediment geochemistry and adjacent drainage basin lithology. The latter case, including this study, was almost always aimed at elucidating the interdependence of different geological processes which may sometimes be screened by the products of forcible human activity. Here, we constructed a tentative model which related the geochemical composition of active stream material in a number of catchments on the Medvednica Mountain, to a broadely defined bedrock lithology which had served as the parent material. The model is a system based, factor model which synthesized eight lithological and 25 geochemical variables (major, minor and trace elements) and reduced their relationships into six geologically meaningful factors. Five of these divulged a definite relationship between geochemistry and lithology. The sixth can be identified as "non-lithologic".

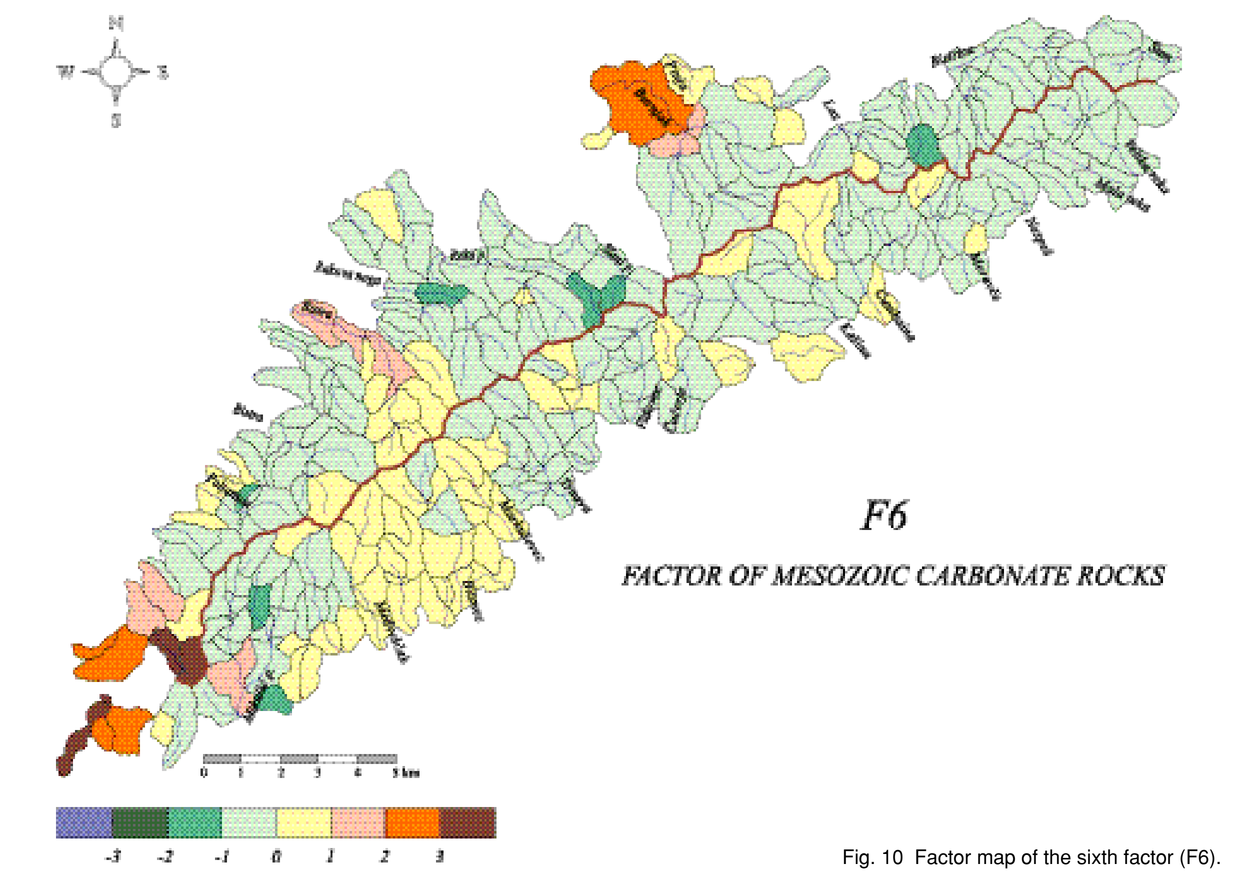

Fig. 10 Factor map of the sixth factor (F6).

Taken together they explain almost two-thirds of the system variability (64%).

Geochemical variables Fe, Ti, Na, V, Co, Zn, Mn, Sc and Y positively correlate to the orthometamorphic lithology LIT2 on the first factor F1, except Th which is negatively associated. This grouping is a result of geochemical composition characterizing the orthometamorphic rocks. The absence of positive correlation of the same variables to basic igneous rocks (with a very similar geochemical composition as the former) could be considered as the effect of the proportionately lower occurrence of igneous rocks in total drainage basin lithology (the effect of dilution - igneous-sedimentary complex!).

The second factor F2 with Ni, Co, Cr, Cu, (Zn), and (As) does not directly associate with any of the proposed lithologic units. This may be either the result of the strong mixing of different lithologies within the stream sediment material (e.g. Co is as strongly loaded to this factor as to the F1) or the enrichment via the ore minerals appearing in the orthometamorphic complex. The third possibility is seen in contamination (quarry, vineyards, etc.).

As anticipated, the elements K, Ba, Th, La and Nb on the factor F3 (factor of igneous rocks) are negatively associated with igneous lithology LIT3. The anomalous factor score values over the areas with parametamorphic lithology (LIT1), as well as Mesozoic carbonate lithology (LIT4), indicate the older, more acid igneous rocks as the source material in their formation.

The fourth factor F4, hosting two dominant geochemical variables, Ca and Sr, and only one lithologic variable, the Tertiary carbonate rocks, in mutually positive correlation, entirely conforms with the chemical composition of the latter (bioclastic and bioaccumulated limestones).

Phosphorus as the dominant element in the F5 (factor of parametamorphic rocks) is related to the accessory component in these rocks (apatite). Negative correlation of this element to the Mesozoic clastic rocks (LIT4) is probably imposed by their original composition.

The Mesozoic carbonates are mostly built of dolomites and dolomitized limestones which is quite clear in F6 from the high positive correlation of Mg with LIT6 lithological group.

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